



Solid-liquid equilibrium of binary and ternary systems formed by ethyl laurate, ethyl palmitate and dodecylcyclohexane: Experimental data and thermodynamic modeling



Maria Dolores Robustillo ^a, Antonio José de Almeida Meirelles ^b,
Pedro de Alcântara Pessoa Filho ^{a,*}

^a Department of Chemical Engineering, Engineering School, University of São Paulo (USP), Caixa Postal 61548, 05424-970, São Paulo, SP, Brazil

^b Department of Food Engineering (DEA), School of Food Engineering (FEA), State University of Campinas (UNICAMP), Rua Monteiro Lobato, 80, 13083-862, Campinas, SP, Brazil

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ABSTRACT

The solid-liquid equilibrium diagrams of binary and ternary mixtures formed by dodecylcyclohexane and the fatty acid esters ethyl laurate and ethyl palmitate was determined herein. The *liquidus* and *solidus* lines were obtained through differential scanning calorimetry. The thermograms of pure compounds were resolved into the corresponding overlapping peak components by a fitting analysis, allowing a better estimation of phase-change properties of polymorphs. All binary systems show immiscibility in the solid phase, although those containing dodecylcyclohexane present small regions of partial miscibility. The system formed by ethyl palmitate and dodecylcyclohexane presents a peritectic transition, which was also observed in the ternary system. The thermodynamic modeling was conducted using different models for liquid-phase non-ideality and considering different polymorphs in solid phase. The modeling shows that a probable inversion of polymorphs relative stability occurs for the binary system formed by ethyl laurate and dodecylcyclohexane. The results from this work may contribute to enhancing the understanding and description of the complex behavior of biodiesel/diesel mixtures at low temperatures.

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1. Introduction

Biodiesel is basically a mixture of fatty acid alkyl esters obtained by the transesterification reaction between fats or oils and alcohol in alkaline medium. It is considered a promising fuel mainly for environmental reasons, but its use at low temperatures is limited by the crystallization of its components, which may lead to flow assurance problems and/or damage of engines. To mitigate this problem, biodiesel is commonly blended with conventional diesel, and flow improvers are added to control its cold properties. The reliable prediction of solid-liquid equilibrium (SLE) by thermodynamic models becomes relevant in those cases. However, the scarcity of experimental data to check their reliability is an important factor that hinders model predictions. Many authors have analyzed melting temperatures of pure fatty acid esters [1]

and their binary or ternary mixtures. It is worth to mention the initial works of Francis and Piper [2], Lockemann and Schlünder [3], and Costa et al. [4], where mixtures of methyl esters were analyzed; the work of Lutton and Hugenberg [5] was focused on the analysis of the behavior of mixtures of both methyl and ethyl esters such as ethyl stearate and methyl stearate. Smith [6], Boros et al. [7] and Costa et al. [8] analyzed mixtures of ethyl esters with ethyl stearate and ethyl palmitate. Imahara et al. [9] and Coutinho et al. [10] analyzed more complex mixtures of biodiesel. Robustillo et al. [11–14] studied ternary mixtures of ethyl esters. Recently, Carareto et al. studied some of these systems at high pressure [15]. Nevertheless, to the best of our knowledge, only a few solid-liquid phase diagrams of mixtures of fatty acid esters and diesel components have been obtained. These phase diagrams include mixtures of ethyl myristate and p-xylene, studied by Collinet and Gmehling [16], and mixtures of fatty acid methyl esters with heavy alkanes and aromatics, studied by Benziane et al. [17,18].

This work continues our previous research on solid-liquid equilibrium of ethyl esters [11–14]. It comprises the experimental

* Corresponding author.

E-mail address: pedro.pessoa@poli.usp.br (P.A. Pessoa Filho).

determination of solid–liquid equilibrium of binary and ternary mixtures of ethyl laurate and ethyl palmitate, two ethyl esters found in biodiesel produced from ethanol [9], and dodecylcyclohexane, a naphthenic compound representative of the naphthenic fraction of conventional diesel [19]. Mixtures were analyzed by differential scanning calorimetry (DSC), which allows the simultaneous determination of both the *liquidus* and the *solidus* lines. Properties of polymorphs of pure compounds were obtained by integrating the corresponding heating thermograms following a method previously proposed by Canotilho et al. (1998) [20]. The procedure consists of picking multiple peaks representing possible polymorphs in the heating thermogram and fitting them with Gaussian functions. To the best of our knowledge, no other experimental data for the binary systems containing dodecylcyclohexane and for the ternary systems can be found in the literature. The solid–liquid equilibrium was described considering different models for the liquid-phase behavior (ideal mixture, Flory–Huggins [21] and UNIFAC-Dortmund [22–24]), and considering different polymorphs in the solid phase.

2. Experimental section

2.1. Materials

Sources and purities of ethyl laurate (1), dodecylcyclohexane (2) and ethyl palmitate (3) are presented in Table 1. The differential scanning calorimeter (DSC 8500 model of Perkin Elmer) was calibrated using indium, naphthalene, cyclohexane and n-decane. The purities and sources of these compounds are also presented in Table 1. Masses were measured in a Sartorius balance with a precision of 0.1 mg.

2.2. Methods

The procedure for obtaining the temperature profile through Differential Scanning Calorimetry (DSC) was the same as used in previous works [11–14]. Briefly:

- (1) Between 2 and 5 mg of the mixture were weighted and placed in hermetic aluminum pans.
- (2) The sample was heated to approximately 15 K above the highest pure component melting temperature.
- (3) The sample was cooled (at a cooling rate of 1 K min⁻¹) to approximately 25 K below the lowest pure component melting point and equilibrated at that temperature for 10 min.
- (4) The sample was heated (at a heating rate of 1 K min⁻¹) until complete melting.

Nitrogen (99.99% purity) was fed at a rate of 50 mL min⁻¹. The transition temperature corresponding to the phase change (melting temperature) was considered to be the transition peak apex, which

is located by the intersection of the tangents to the peak slopes. It corresponds to the absolute minimum of the heat flow in the heating thermogram for every phase change signal considered. In general, the melting temperature matches the highest temperature transition observed in the thermogram; exceptions due to overlapped peaks will be explained in the Results section.

3. Modeling

Phase equilibrium was studied by means of a stability analysis following the procedure previously developed by Barbosa and Pessôa Filho [25]. According to this method, the *liquidus* line temperature corresponds to the onset of the formation of a solid phase, for a certain liquid phase composition. It can thus be calculated through a stability analysis.

For eutetic systems, the stability analysis leads to the usual solid–liquid equilibrium equations. If peritectic reactions occur, the temperature of the *liquidus* line (T) can be calculated through [25] assuming that the peritectic compound formed by the reaction between compounds i and j corresponds to a 1:1 compound:

$$\left(\frac{\Delta_{fus}G_i}{RT} + \ln(a_i^L)\right) + \left(\frac{\Delta_{fus}G_j}{RT} + \ln(a_j^L)\right) + \ln(K_{ij}) = 0 \quad (1)$$

wherein $\Delta_{fus}G$ is the Gibbs energy change on fusion, K_{ij} is the equilibrium constant of the peritectic reaction between i and j and its logarithm can be also written as a linear function of temperature:

$$\ln(K_{ij}) = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{R} \left[\frac{1}{T}\right] + \frac{\Delta S^0}{R} = \frac{b}{T} + a \quad (2)$$

wherein ΔH^0 and ΔS^0 are the standard enthalpy and entropy associated to the peritectic reaction, respectively.

To calculate the activity of compounds in liquid phase, three approaches were considered. The first one is to consider that the liquid phase is ideal. The second one is to consider that the liquid-phase non-ideality is given by the Flory–Huggins equation [21]:

$$\ln(a_i^L) = 1 + \ln(\phi_i) - v_i \sum_j \frac{\phi_j}{v_j} + v_i \left(\sum_j \chi_{ij} \phi_j - \sum_j \sum_{k>j} \chi_{jk} \phi_j \phi_k \right) \quad (3)$$

Volume fractions are calculated through:

$$\phi_i = \frac{x_i v_i}{\sum_j x_j v_j} \quad (4)$$

and the summations are carried out over all the compounds. To calculate the volume fractions, UNIFAC-Dortmund volume parameters were used as molar volumes [22].

Table 1
Sources and purities of compounds used in the experiments.

Chemical name	Source	Mass fraction purity
Ethyl laurate	Sigma Aldrich	≥0.98
Ethyl palmitate	Sigma Aldrich	≥0.99
Dodecylcyclohexane	TCI America	≥0.98
Indium ^a	Perkin Elmer (calibration standard)	0.9999
Naphthalene ^a	Merck	≥0.99
Cyclohexane ^a	Merck	≥0.99
n-decane ^a	Sigma Aldrich	≥0.99

^a Compounds used only for calibrating the DSC apparatus.

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